SYNTHETIC METHODS FOR POLYPYRIDINES

BY

EDWARD FRANCIS RIENER

B.S., Ursinus College, 1947
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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SYNTHETIC METHODS FOR POLYPYRIDINES

Introduction

A study of polypyridines as insecticides reveals that those possessing a structure similar to nicotine, *i.e.*, the 2,3′-linkage, are often as effective as nicotine itself. It is also well known that polypyridines having 2, 2′-linkages have the ability to chelate with metals and form complexes. The preparation of a series of substituted polypyridines which have 2,3′-linkages or 2,2′-linkages would be of extreme interest because this would permit the comparative study of such a series in order to determine the effect of the substituents.

The Tschitschibabin reaction has been used to prepare alkyl and aryl substituted pyridines (1). This method involves heating a mixture of one mole of aldehyde, two moles of ketone and a tenfold excess of ammonia as ammonium hydroxide with a small amount of ammonium acetate as catalyst in a sealed autoclave at 250° for three hours. Thus, the use of a pyridyl-substituted ketone or aldehyde in the Tschitschibabin reaction presented itself as a new approach to the synthesis of polypyridines. This research was undertaken to determine the scope and limitations of the Tschitcshibabin reaction for the synthesis of polypyridines.

Discussion Of Results

The method was found applicable for the preparation of a variety of polypyridines in 23 to 32 per cent yields. The polypyridines prepared for pharmacological study are as follows:

a. 2,6-di-(3-pyridyl)-4-phenylpyridine

b. 2,4,6-tri-(3-pyridyl)-pyridine

c. 2,6-di-(2-pyridyl)-4-phenylpyridine

d. 2,6-di-(3-pyridyl)-3,5-di-(2-pyridyl)-4-phenylpyridine

e. 2,6-di-(3-pyridyl)-3,4,5-triphenylpyridine

f. 3,5-di-(2-pyridyl)-2,4,6-triphenylpyridine

The unequivocal synthesis of 2,6-di-(2-pyridyl)-4-phenylpyridine by the condensation of hydroxylamine and benzaldi-(2-acetylpyridine) was further evidence for the mechanism as previously postulated that the aldehyde group is introduced at the *gamma* position of the newly formed pyridine nucleus.

Attempts to prepare 2,6-di-(2-pyridyl)-4-phenylpyridine by the usual method in the autoclave were unsuccessful. This was probably due to the chelation of the 2,2′,2″-polypyridine with the metal from the autoclave. However, it was prepared in good yield by heating the mixture in a sealed glass tube placed in the autoclave.

Extensive study of the reaction revealed two primary limitations:

1. The starting ketones must be identical or else mixtures results.
2. The aldehyde must be aromatic. The use of alkyl aldehydes or formaldehyde does not produce the desired pyridine.

The low yields (5.4 per cent) of 3,5-di-(2-pyridyl)-2,4,6-triphenylpyridine and 2,6-di-(3-pyridyl)-3,5-di-(2-pyridyl)-4-phenylpyridine revealed another limitation.

3. A lower yield of polypyridine results when the ketone used has a structure related to that of 2-phenacylpyridine. The heat, pressure and strong alkaline conditions of the reaction cleave the ketone, which resembles a 1,3-diketone.

A simple method for the preparation of pyridyl aldehydes would be very desirable. An unsuccessful attempt was made to utilize the Schmidt reaction (2), *i.e.*, the action of hydrazoic acid with olefins, as a means of obtaining various pyridyl aldehydes. Considerable tar and polymer resulted when

2-styrylpyridine or 2-vinylpyridine was treated with hydrazoic acid, probably due to the hydrazoic acid acting as the HN free radical.

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VITA

The author was born in Philadelphia, Pennsylvania on September 16, 1924, where he received his elementary and high school education. He was sent to Ursinus College, Collegeville, Pennsylvania from July, 1943 to July, 1945, under the auspices of the Navy Training Program. After he was discharged from the Navy in 1946, he returned to Ursinus College and received the degree of Bachelor of Science there in 1947. At this time, he entered the Graduate College at the University of Illinois. He was a University of Illinois Fellow in Chemistry from September, 1948 to June, 1950, and a Research Assistant from October, 1950, to February, 1951.

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